

## O 10: Organic Molecules on Inorganic Substrates II: Electronic, Optical and Other Properties II

Time: Monday 15:00–17:30

Location: CHE 89

**Topical Talk**

O 10.1 Mon 15:00 CHE 89

**Photoemission Orbital Tomography: Imaging Molecular Wave Functions in Reciprocal and Real Space** — ●F. S. TAUTZ — Quantum Nanoscience, Peter Grünberg Institute (PGI-3), Forschungszentrum Jülich, Germany

The photoemission orbital tomography (POT) technique, a variant of angle-resolved photoemission spectroscopy, has been very useful in the characterization of the electronic properties of molecular films. It is a combined experimental and theoretical approach that is based on the interpretation of the photoelectron angular distribution in terms of a one-electron initial state. This includes the unambiguous assignment of emissions to specific molecular orbitals, their reconstruction to real space orbitals in two and three dimensions, the deconvolution of complex spectra into individual orbital contributions beyond the limits of energy resolution, the extraction of detailed geometric information such as molecular orientations, twists and bends, the precise description of the charge balance and transfer at interface, and the detection of momentum-selective hybridization with the substrate, to name only a few examples. In its simplest form, POT relies on the plane-wave approximation for the final state. While this works surprisingly well in many cases, this approximation does have its limitations, most notably for small molecules and with respect to the photon-energy dependence of the photoemission intensity. Regarding the latter, a straightforward extension of the plane wave final state leads to a much-improved description while preserving the simple and intuitive connection between the photoelectron distribution and the initial state.

O 10.2 Mon 15:30 CHE 89

**Structural Reorientation of Organic Molecules on Surfaces by Alkali Metal Doping** — ●RALF HEMM<sup>1</sup>, KA-MAN YU<sup>1</sup>, STEFFEN-RAMBERT ROTHENBERG<sup>1</sup>, SERGEY SOUBATCH<sup>2</sup>, CHRISTIAN KUMPF<sup>2</sup>, MARTIN AESCHLIMANN<sup>1</sup>, and BENJAMIN STADTMÜLLER<sup>1,3</sup> — <sup>1</sup>RPTU Kaiserslautern-Landau, Erwin-Schrödinger-Str. 46, 67663 Kaiserslautern, Germany — <sup>2</sup>Peter Grünberg Institut, Forschungszentrum Jülich, 52425 Jülich, Germany — <sup>3</sup>Johannes-Gutenberg-Universität Mainz, Staudingerweg 7, 55128 Mainz, Germany

Organic semiconductors are promising materials for the fabrication of next-generation organic-based electronic devices. The electron properties of the organic thin film can be tuned by alkali metal doping and the consequent charge transfer. Here, we study the influence of Cs doping on the structural and electronic properties of the model system PTCDA/Ag(111). Using momentum microscopy, we can simultaneously access changes in occupation of the molecular orbitals and determine modifications of the azimuthal orientation of the PTCDA molecules upon Cs doping. We can identify two structural Cs-PTCDA phases depending on the Cs concentration with either one or two Cs atoms per PTCDA. With increasing Cs concentration, we observe a gradual structural reorientation of the molecules that is accompanied by a modification of the population of the molecular states. Both cases are different from the pristine case. The structural reorientation of the PTCDA molecules can be attributed to the electrostatic interactions between the partially ionized Cs atoms and the negatively polarized oxygen end groups of PTCDA.

O 10.3 Mon 15:45 CHE 89

**Tip-enhanced Raman Spectroscopy of a charged molecule** — ●RODRIGO CEZAR DE CAMPOS FERREIRA<sup>1</sup>, JIŘÍ DOLEŽAL<sup>1,2</sup>, AMANDEEP SAGWAL<sup>1,2</sup>, SOFIA CANOLA<sup>1</sup>, and MARTIN ŠVEC<sup>1,3</sup> — <sup>1</sup>Institute of Physics, Czech Academy of Sciences; Czech Republic — <sup>2</sup>Faculty of Mathematics and Physics, Charles University; Czech Republic — <sup>3</sup>Institute of Organic and Inorganic Chemistry, Czech Academy of Sciences; Czech Republic

The Tip-enhanced Raman spectroscopy (TERS) technique has been proven to unveil fundamental features of single molecules at the nanoscale level via near-field spectroscopy [1,2]. The confined light in the STM junction can be used as a probe to obtain an essential understanding of molecular structure and electronic properties. Here, the LT-STM-controlled TERS technique was performed and verified for the perylene tetracarboxylic dianhydride (PTCDA), which was measured the Raman fingerprint for a single molecule on Ag(111) and on insulating NaCl/Ag(111) from different excitation sources. Moreover, the precise control of geometry and charge state of the molecule in

the system [3] can be observed together with the Raman fingerprint and revealed an abrupt change in the spectra. We correlate them to the presence of Kondo signature and discuss the implication for other systems.

[1] R. Zhang et al., *Nature*. 2013, 498, 82-86 [2] J. Lee et al., *Nature*. 2019, 568, 78-82 [4] M. Žonda et al., *J. Phys. Chem. Lett.* 2021, 12, 6320

O 10.4 Mon 16:00 CHE 89

**Charge-induced symmetry breaking in the adsorption configuration of C60 layers on h-BN/Ni(111)** — ●MAX BOMMERT, ROLAND WIDMER, NÉSTOR DIEZ, BRUNO SCHULER, and OLIVER GRÖNING — Empa \* Swiss Federal Laboratories for Materials Science and Technology, 8600 Dübendorf, Switzerland

Hexagonal Boron Nitride (h-BN) and Nickel's (111) surface share a nearly perfectly matching lattice constant. Consequently, monolayer h-BN can be grown commensurately on Ni(111) without exhibiting a Moiré superstructure like on many other h-BN/transition metal systems. Nevertheless, upon adsorption at room temperature and scanning tunneling microscopy (STM) imaging at 5K, we observe a complex, geometrically frustrated adsorption pattern for sub-monolayer C60 coverages. The fullerenes form large molecular islands with a distinct striped pattern that we can identify as C60 adsorbed in different orientations. We use scanning tunneling spectroscopy (STS) to resolve the lowest unoccupied molecular orbitals (LUMO) of the C60. Tip-induced manipulation of single molecules affects the LUMO energy of neighboring molecules. Based on our STS investigations, we propose a significant charge transfer from the substrate to specific C60 and the associated electrostatic repulsion to be a driving force in forming the stripe pattern. We rationalize the latter by Monte Carlo simulations of the C60 lattice, considering the various contributions to the intermolecular and molecule-substrate interactions. Our results deepen the understanding of molecular adsorption and charge transfer processes, which are crucial for developing organic-inorganic hybrid devices.

O 10.5 Mon 16:15 CHE 89

**Nickel(II) Porphyrins versus Nickel(II) Corroles on Different Metal Surfaces: Oxidation-State Tuning of Nickel Tetrapyrrole Complexes** — ●JAN HERRITSCH<sup>1</sup>, JAN-NICLAS LUY<sup>1,2</sup>, RALF TONNER-ZECH<sup>1,2</sup>, and J. MICHAEL GOTTFRIED<sup>1</sup> — <sup>1</sup>Fachbereich Chemie, Philipps-Universität Marburg, Germany — <sup>2</sup>Wilhelm-Ostwald-Institut, Leipzig, Germany

Using the example of Ni tetrapyrrole complexes, we demonstrate how the oxidation state of the central atom and the molecule-substrate interaction can be influenced by a modification of the ligand. In particular, the effect of the ring size is addressed by comparing porphyrins with corroles. The latter represent a smaller macrocycle and provide a tighter coordination environment for the metal center. In addition, Ni(II) corroles have an unusual electronic structure with an unpaired electron located at the  $\pi$ -electron system of the ligand. Here, we focus on the interactions of Ni(II) porphyrins and corroles with different metal surfaces (Au(111), Ag(111), Cu(111)). Depending on the used substrate, the Ni(II) porphyrin is subject to an interfacial charge transfer resulting in the reduction of the Ni atom as was shown by XPS. However, due to its unique properties Ni(II) corroles exhibit a different behavior at the metal/organic interface. While the corrole's Ni(II) state remains unchanged even on the reactive Cu(111) surface, the ligand is subject to a charge transfer by accepting electron density from the substrate. This charge transfer could be traced with experimental valence spectra (UPS), which were evaluated with the help of quantum chemical calculations (DFT).

O 10.6 Mon 16:30 CHE 89

**Electronic Properties of N-Heterotriangulene Derivatives adsorbed on Au(111)** — ●JAKOB STEIDEL<sup>1</sup>, INA MICHALSKY<sup>2</sup>, MILAN KIVALA<sup>2</sup>, and PETRA TEGEDER<sup>1</sup> — <sup>1</sup>Institute of Physical Chemistry, Heidelberg University, Im Neuenheimer Feld 253, 69120 Heidelberg — <sup>2</sup>Institute of Organic Chemistry, Heidelberg University, Im Neuenheimer Feld 270, 69120 Heidelberg

A large number of opto-electronic devices based on organic compounds utilize donor-acceptor-systems (D-A-systems), for example as the emitting layer in organic light emitting diodes or for charge separation in organic photovoltaics. Triphenylamine and its derivatives are a class

of donors in D-A-systems with a high potential for applications in devices.

Introducing an etheno-bridge in the planar triphenylamine derivative indolo[3,2,1-jk]carbazole (N-heterotriangulene-550, N-HTA-550) closes an antiaromatic ring with seven members in the resulting N-heterotriangulene-557 (N-HTA-557). This significantly changes the electronic structure while retaining the molecular geometry as well as the steric demands. By oxidation of N-HTA-557 and a subsequent condensation reaction with quinoxaline-2,3-diamine an intramolecular D-A-system is created.

In the present contribution we study the electronic properties of N-HTA-550 and its derivatives on a Au(111) surface using two-photon photoemission spectroscopy.

O 10.7 Mon 16:45 CHE 89

**Influence of N-introduction in pentacene on the electronic structure** — ●MOHSEN AJDARI<sup>1</sup>, MARVIN HOFFMANN<sup>2</sup>, FELIX LANDWEHR<sup>1</sup>, OLENA TVERSKOY<sup>3</sup>, UWE H. F. BUNZ<sup>3</sup>, ANDREAS DREUW<sup>2</sup>, and PETRA TEGEDER<sup>1</sup> — <sup>1</sup>Physikalisch-Chemisches Institut — <sup>2</sup>Interdisziplinäres Zentrum für Wissenschaftliches Rechnen — <sup>3</sup>Organisch-Chemisches Institut, Universität Heidelberg

Organic electron-transporting (n-channel) semiconductors such as N-heteropolycyclic aromatic compounds are of great interest for use in a variety of (opto)electronic applications.

In this study, vibrational and electronic high-resolution electron energy loss spectroscopy (HREELS) in combination with quantum-chemical calculations are utilized to investigate the influence of N-introduction on the adsorption geometry and electronic structure of two pentacene derivatives, namely 6,13-diazapentacene (DAP) and 6,7,12,13-tetraazapentacene (TAP) on Au(111).

Our findings indicate that in comparison to parent pentacene (PEN), introduction of nitrogen atoms in the aromatic backbone of its aza derivatives leads to a narrowing of the optical gap ( $S_0 \rightarrow S_1$  transition) from 2.1 eV for PEN to 2.0 eV for DAP and to 1.6 eV for TAP as well as an increase in the first triplet state energy from 0.9 eV for PEN and DAP to 1.2 eV in TAP. Additionally, in the series PEN, DAP, and TAP, the  $\alpha$ -band ( $S_0 \rightarrow S_2$  transition) gains significantly in intensity due to individual effects of the introduced nitrogen atoms on the orbital energies.

O 10.8 Mon 17:00 CHE 89

**Electrostatic design of the internal surfaces of porous organic materials** — ●EGBERT ZOJER — Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Austria

Collective electrostatic effects are ubiquitous at surfaces and interfaces involving organic materials. [1] Thus, they, for example, allow tuning the electronic properties of interfaces employing monolayers of molecules with embedded dipoles [2]. This raises the question, whether controlled assemblies of dipoles couldn't also be used to control the properties of the inner surfaces of porous structures. This question is addressed for the prototypical case of layered covalent organic frameworks that are stacked in a way that 1D channels are formed. Employing state-of-the-art quantum-mechanical simulations, it is shown that by changing the polarity of the functional groups covering the surfaces of these pores, the electrostatic energy in the pores can be changed by more than one eV in a comparably straightforward manner. As this energy crucially determines the interaction between the host material and adsorbates within the pores, the proposed strategy holds the promise of revolutionizing various fields of application of such materials, e.g., as battery electrodes, in catalysis, and in excited-state charge separation processes. [1] E. Zojer, T. C. Taucher, and O. T. Hofmann, *Adv. Mater. Interf.* (Hall of Fame Review), 1900581 (2019); [2] E. Zojer, A. Terfort, and M. Zharnikov, *Acc. Chem. Res.* 55, 1857 (2022)

O 10.9 Mon 17:15 CHE 89

**Screening Non-alternant  $\pi$ -Electron Systems for Metal-Organic Interfaces: Interplay between Topology, Aromaticity, and Adsorption Behavior** — ●JAKOB SCHRAMM and RALF TONNER-ZECH — Universität Leipzig, Deutschland

Metal-organic interfaces play an important role in organic electronics. Topology, aromaticity, and interface properties are closely connected here as previously shown by experimental and theoretical studies of isomer pairs of alternant and non-alternant adsorbates. While non-alternant azulene and azupyrene chemisorb on Cu(111), the alternant isomers naphthalene and pyrene physisorb.[1,2] This promises to be a general trend and can be exploited for interface design.

Here, we report data based on periodic DFT calculations for a set of 11 non-alternant molecules in comparison to analogous alternant molecules. Influence of topology on atomic and electronic structure, especially aromaticity, was analyzed based on molecular gas phase calculations. Interface properties were then derived using slab approaches at the example of Cu(111). We report on the interplay of topology and adsorption structure, adsorption energy, and charge transfer.

[1] B. P. Klein, R. Maurer, R. Tonner, C. Kumpf, I. Swart, J. M. Gottfried et al., *Phys. Rev. X* 2019, 9, 011030; [2] B. P. Klein, R. Maurer, G. Hilt, R. Tonner-Zech, A. Schirmeisen, J. M. Gottfried et al., *ACS Nano* 2022, 16, 11979-11987.